Evidence for Site-Specific Empirical Partition Coefficient (K_d) for the Rocky Flats Environmental Technology Site (RFETS)

Purpose

This report will briefly discuss:
- The definition of an empirical partition coefficient (K_d);
- The use of Site-specific empirical K_ds, in transport modeling; and
- The range of empirical K_ds that have been determined using contaminated soils and sediments from RFETS.

This report will not discuss:
- Whether the use of empirical K_ds in groundwater modeling is appropriate;
- The adequacy of the current model used for estimating surface soil action levels; and
- The effects of Pu speciation or changing environmental parameters on the K_d.

The Empirical K_d for Use in Groundwater Transport Modeling

The empirical K_d, also known as an *in-situ*, apparent or effective K_d, as used in groundwater modeling calculations, is defined as "the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium" (EPA, 1999). For radionuclides an equation to calculate an empirical K_d looks like:

$$K_d \ (\text{ml/g}) = \frac{C_{\text{I Particulate}} \ (\text{pCi/g})}{A_{\text{I Aqueous}} \ (\text{pCi/ml})}$$

Where C_I is the initial activity-concentration of the radionuclide in the particulate or solid phase, A_I is the activity-concentration of the radionuclide in the aqueous phase at equilibrium.

This *empirical unit of measure* may be determined in a number of ways, both in the laboratory and the field. The empirical or apparent K_d is a measure of the behavior of an element under specific environmental or laboratory conditions. It is not a constant. The empirical K_d reflects the response of the element to all of the many variables that effect its interaction with the solid and aqueous phases with which it is in contact. It is a site-specific and environment-specific parameter. Empirical K_d values developed at one site or under one set of laboratory or field conditions can not easily be transferred to another site due to environmental differences including: climate, soils, mineralogy, microenvironment, and contaminant source materials. The empirical K_d for an element may vary at a particular site depending on changes in the micro-environment. Ideally, only site specific empirical K_d values should be used for site-specific contaminant transport calculations.

The Use of Empirical K_ds in Contaminant Transport Modeling.

Currently the most common approach to modeling the transport of contaminants in the aqueous phase is the K_d model. It is a simplistic approach that uses the K_d as an empirical metric that accounts for many chemical, physical, and even biological processes that are influenced by innumerable variables. The empirical K_d is used as a simplifying assumption and descriptor for very complex systems. Therefore, the robustness of the empirical K_d used in a model to determine the movement of contaminants in a given environment depends on the care that has been taken to ensure that the K_d is truly representative of various conditions that could be encountered along the flow-path. If conditions change significantly, multiple K_ds can be used, f allowed by the model.
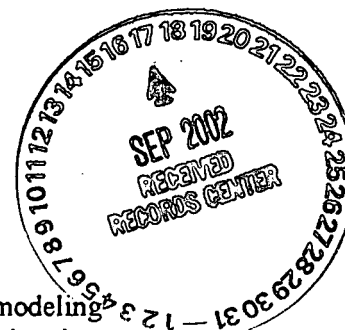
More complex methods are in use. They can be based on geochemical models that account for changes in mineralogy and aqueous chemistry in the modeled system, and/or mechanistic models that account for variables affecting surface adsorption on soil particles. These types of models will become dominant as the knowledge of the complex interactions that occur among soil particulates, the aqueous phase, variables such as eH and pH, and the myriad chemical species present, and, possibly even more importantly, the computer technology becomes available to easily create and use such complex models.

K_ds and Site–Specific Action Levels

The RESRAD model, developed by the Argon National laboratory, is currently being used to calculate dose-based action levels for radionuclides at RFETS. The RESRAD model uses the K_d approach to calculate the rate of movement of radionuclides from the source, through the soil to the saturated zone and then, in the saturated zone. Documentation for the model recommends the use of a site-specific K_d, whenever possible and cautions against the use of default values and values developed at other sites.

The K_d values are important in the RESRAD model for RFETS because they determine the rate at which the radionuclide contaminants are leached from the surface soil, to groundwater. Therefore, over periods of hundreds of years that are modeled, the K_d can control which exposure pathways dominate and the doses a receptor may receive from various pathways.

RFETS-Specific Empirical K_ds

Many observations on the movement of Pu and americium (Am) in the soils of RFETS and estimates of Site-specific empirical K_ds have been made over the years. In the 1970's, studies were done by Krey and Hardy with others (1970, 1976, 1977) and Little (1978, and 1980) on the depth distributions of Pu and Am from the 903 Pad source area. They found that the Pu and Am had redistributed in the soil profile over the course of 4 to 7 years so that about 60% of the inventory was in the top 5 centimeters (cm) and that the activity-concentration decreased exponentially with depth in the soil profile.

Some of the same areas were sampled by Webb (1992) in 1989. He found that the depth distributions determined in 1989 were statistically indistinguishable from those determined in the early 1970's. Similar distributions were documented by Litaor et al. (1994, DOE 1995). The fact that depth distributions for Pu and Am in soils at Rocky Flats have not changed significantly over more than twenty years indicates that the contamination moved quickly after release to the soil environment to form an exponential depth distribution in the soil profile and then has stayed relatively static over the intervening years. This behavior may be due to changes in chemical form (speciation) after contact with the soil environment that effected solubility and/or may be due to the formation of associations with soil mineral and organic constituents. The importance of this information , is that *it is a strong indication* that Pu and Am, in their current form in the soils of RFETS, move vertically in soils only very slowly. Therefore, a relatively high Site-specific empirical K_d value is appropriate for Pu and Am in the surface and near surface soils of RFETS.

Cleveland et al. (1976) determined distribution coefficients for Pu and Am at a range of pH values for pond sediments at RFETS. They determined: 1) that 82% of the Pu and 76% of the Am was associated with the 4.6 to 13 micrometer (μm) sediment sizes; 2) that Pu and Am were released in increasing quantities as pH increased; 3) that Pu and Am existed primarily as colloids that decreased in size with increasing pH; and 4) that after an initial release to the aqueous phase the Pu and Am gradually redeposited on the sediments. Table 1 shows the Pu and Am empirical K_ds determined for over a range of pH. These samples were not filtered, but centrifuged at 5000 rpm 5 minutes. Thus, these estimates represent a lower bound. At environmental pHs found at RFETS (pH 6 to 8) the empirical K_d ranged

from 3.6×10^4 ml/g to 2.4×10^5 ml/g and were dependent on both pH and extraction time. Figures 1 and 2 show that with longer extraction times the values for all pHs shown converge near 10^5.

Table 1. Pu and Am Empirical Partition Coefficients for RFETS Pond Sediments (ml/g)

Pu Empirical Partition Coefficients for RFETS Pond Sediments (ml/g)						
PH	2 hr	4hr	8hr	20hr	34hr	68hr
5	312500	121951	185185	500000	196078	45249
6	232558	243902	103093	144928	161290	108696
7	116279	76336	192308	161290	105263	125000
8	36101	59524	82645	100000	73529	91743
9	11547	6707	8006	12285	39683	52356
Summary Statistics for pH 6 to 8						
	Maximum	243902				
	Minimum	36101				
	Average	118343				
	Standard Deviation	57264				

Am Empirical Partition Coefficients for RFETS Pond Sediments (ml/g)						
PH	2 hr	4hr	8hr	20hr	34hr	68hr
5	153846	106383	153846	344828	111111	30303
6	NA	135135	135135	78740	74074	68493
7	181818	62893	200000	151515	69444	53476
8	20661	25707	59172	48780	38610	45662
9	7358	5198	4625	9615	19342	39216
Summary Statistics for pH 6 to 8						
	Maximum	200000				
	Minimum	20661				
	Average	85254				
	Standard Deviation	54508				

The values determined by Cleveland compare very well with other values determined using RFETS sediments and soils. Litaor (1998) determined empirical K_d from *in-situ* infiltration experiments conducted in soil pits to the east of the 903 Pad. Values for Pu determined on filtered (0.45 µm) samples ranged from 2.1×10^5 ml/g to 3.1×10^5 ml/g at 0 to 20 cm from the surface (Table 2). Am values were in the same range, varying from 1.4×10^5 ml/g to 3×10^5 ml/g at the 0 to 20 cm depth.

Table 2. Pu and Am Empirical K_d Values from OU-2 Soil Pit Studies

Depth (cm)	Pu (ml/g)	Am (ml/g)
0-20	212000	296000
	311000	141000

Honeyman(1997) developed empirical K_d values for Pu from six surface soil samples taken from the 903 Pad Area. The samples varied by an order of magnitude in Pu activity-concentrations. However, the empirical K_ds developed from laboratory equilibration of the soils with RFETS groundwaters were not related to the soils' activity-concentrations. The solutions were passed through a 0.45 µm filter and ranged from 9.8×10^3

ml/g to 1.4×10^5 ml/g. These findings are consistent with the values those reported for sediments by Cleveland.

Honeyman (1998) reports the results of a sequential extraction study. The first step was to determine "exchangeable" Pu by extracting the soil with KNO_3. Partition coefficients developed from this data should represent a lower bound, due to the high ionic strength of the extracting solution. These partition coefficients for Pu, determined on 0.45 μm filtrate, ranged from 2.2×10^4 ml/g to 4.3×10^4 ml/g for 5 replicates. These values are well within the range for empirical Site-specific K_ds for RFETS.

Honeyman (1999) reported the results of experiments to determine the release of Pu and Am into solution under a range of eH, varying from ambient oxidizing conditions (800mV) to reducing conditions (-90 mV). The empirical K_ds for Pu from this experiment, determined on 0.45 μm filtrate, ranged from 5×10^4 ml/g to 2.8×10^5 ml/g. The values for Pu tended to be higher at lower redox potentials (lower eH). The values for Am ranged from 2.3×10^4 ml/g to 1.5×10^5 ml/g with no effect across redox potentials.

Data have been collected for surface water and at one well from which Site-specific emperical K_d values have been calculated. Empirical K_ds determined on surface waters may not be appropriate to use for groundwater modeling, but give an indication of how changing environmental conditions and factors may effect Pu and Am transport.

Harnish et al. (1996) examined well water (well1587) and seep water (SW51 and SW53) from the 903 Pad area.. Using ultra filtration techniques they found that 65% of the Pu in the aqueous phase was particulate and colloidal. Although they did not calculate empirical K_ds partition coefficients for the suspended solid phase can be developed from the reported data for both 0.45 μm filtrate and for filtrate passing a 10,000 dalton filter (Table 3). The values for the 0.45 filtrate are on the high end of those previously reported. Values for the 10,000 dalton filtrate are higher, as expected, due to removal of colloidal particulates. These values appear to represent an upper bound for empirical K_ds for groundwater.

Table 3. Empirical K_ds for Pu (ml/g) Derived from Harnish et al., 1996

Location	< 0.45 μm	<10,000 dalton
Well 1587	9200000	19000000
SW51	2100000	8000000
SW53	820000	1400000

Santschi (1999) reported empirical K_ds for particulates in surface water from a pond discharge on Walnut Creek and a storm event at GS10 at the eastern edge of the Industrial Area (Table 4). The values for Pu and Am are very similar and well with in the range of previously reported values at RFETS. Values were also reported for work done in 1998. These are not reported here due to the very low activities found in the surface waters.

Table 4. Partition coefficients (K_d, l/kg or ml/g) of Pu and Am.

Isotope	Sampling Date	Location	C_p (mg/l)	K_d (ml/g)
Pu	4/27/99 - Discharge	Walnut Creek	38.8	1.7×10^4
Pu	4/30/99 - Storm event	GS10	120	4.1×10^3
Am	4/27/99 - Discharge	Walnut Creek	38.8	1.3×10^4
Am	4/30/99 - Storm event	GS10	120	7.9×10^3
C_p (mg/l) is the concentration of suspended particulate matter.				

Summary

The data reported herein is a sampling of Site-specific empirical K_d values for Pu and Am, determined for contaminated soils, sediments, groundwater, and surface water at RFETS. This report is not meant to be an exhaustive treatment of all available data, but rather an overview of the range of empirical K_d values that have been reported at RFETS using a variety of methods.

The data reported indicates that:
- Data collected over a period of 25 years indicates that the depth distributions for Pu and Am have not changed over that time. This supports the conclusion that Pu and Am in surface soils at RFETS are relatively immobile.
- The data indicates that Pu and Am behave very similarly under a range of conditions and methods of determination at RFETS;
- Pu and Am Site-specific empirical K_d values sediments, soils, and surface water particulates are in the same range.
- The lower and upper bounds for data reported here are similar under a variety of conditions. Honeyman and Cleveland report lower bounds in the 10^4 ml/g range. Santschi, using surface water samples reports a lower bound of 4×10^4. The highest value for Pu, 10^7 ml/g, was calculated from well water data using the data of Harnish et al. (1996), however, this value is suspect, due to low activities. Most of the data reviewed suggest an upper bounds in the 10^5 range. The variables responsible for the two order of magnitude range in values is not obvious from the data reviewed.

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Figure 1. Effect of Extraction Time and pH on Empirical Partition Coeffiecients for Plutonium in Pond Sediments at RFETS
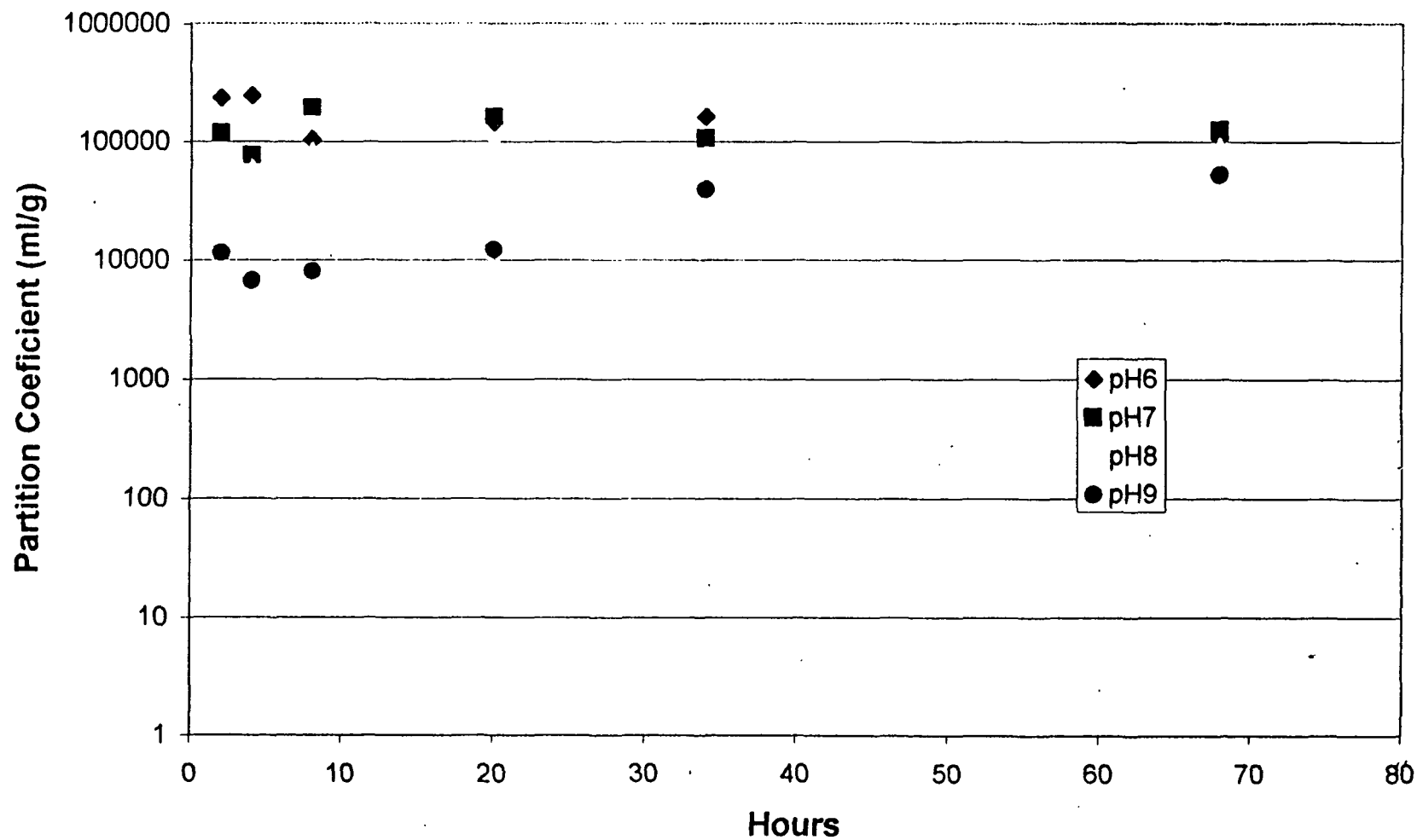

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Figure 2. Effect of Extraction Time and pH on Empirical Partition Coeffiecients for Americium in Pond Sediments at RFETS